THESIS

FREE RADICALS

by

R. R. Grunert, B. Sc.

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FREE RADICALS

by

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A Thesis

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Thesis
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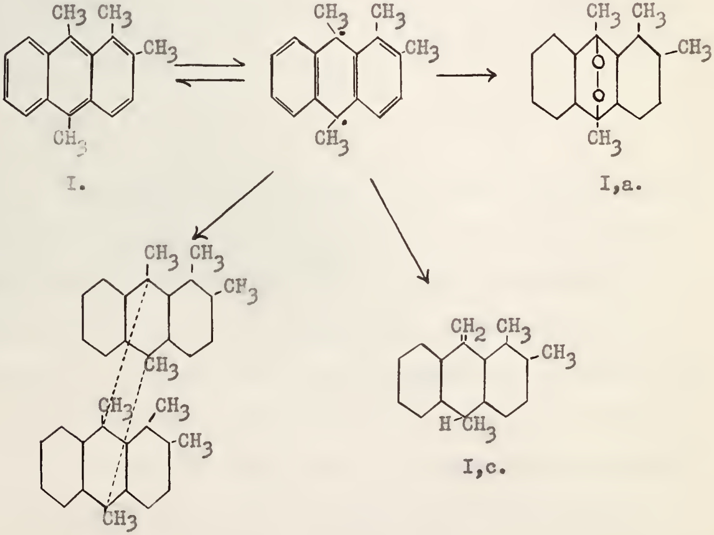
FREE RADICALS

Introduction

1,2,9,10-Tetramethylanthracene (I) was synthesized in 1943 (22). Great difficulty was encountered in obtaining the final product since the compound possessed a great tendency to combine with oxygen from the air to form the peroxide. The conclusion arrived at was that this compound existed as an unstable diradical characterized by a tendency to form a peroxide (I,a), a dimer (I,b) and to undergo dismutation (I,c).



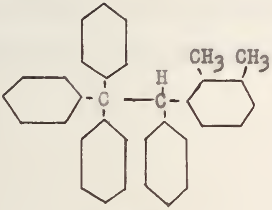
I.

I,a.

I,b.

I,c.

In order to get an insight into the reason for the great reactivity of 1,2,9,10-tetramethylanthracene, the primary object of the research outlined in this thesis was to prepare 1,1,1,2-tetraphenyl-2(3-o-xylyl)ethane (II) and to determine its "half-life" period.



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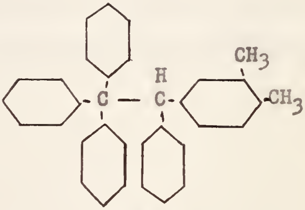

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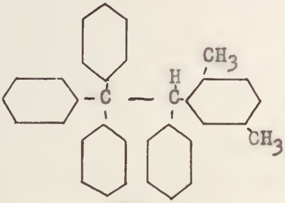

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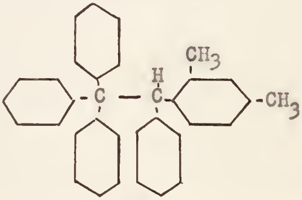


V.

By comparison it was seen that the free radical, obtained by the dissociation of the pentaarylethane II, had a structure similar to the diradical form of I. Therefore, stability data obtained for II should be applicable to I. Great difficulty was encountered in the preparation of II. Hence it was concluded that the two ortho-methyls exerted considerable influence on reactions involving the methane carbon atom. The question then was whether the two methyl groups exerted a similar effect when they were in

other locations.

This research, therefore, expanded itself into the preparation of, and determination of the "half-life" periods of, as many pentaarylethanes as possible, each one containing a xylene group in the diarylmethyl radical. The compounds attempted were 1,1,1,2-tetraphenyl-2(4-o-xylyl)ethane (III), 1,1,1,2-tetraphenyl-2(2-p-xylyl)ethane (IV), and 1,1,1,2-tetraphenyl-2(4-m-xylyl)ethane (V).

Theory of Free Radicals

I. History

Up to 1900 free radicals had been discussed by such workers as Lavoisier, Bunsen, Frankland, Cannizzaro and Ostwald, but free radicals had not been isolated.

In 1900 Gomberg (1)(2) succeeded in synthesizing hexaphenylethane. By heating a benzene solution of triphenylchloromethane with silver he obtained a colorless solid with a high melting-point and a low solubility.

$$2(C_6H_5)_3C\text{-}Cl + 2\ Ag \longrightarrow 2\ AgCl + (C_6H_5)_3C\text{-}C(C_6H_5)_3$$

Repeated analysis, however, indicated the presence of oxygen. By running the reaction in an atmosphere of carbon dioxide, he showed that this oxygen came from the air. Under these conditions the oxygen compound did not form and evaporation of the solution yielded a hydrocarbon whose composition corresponded to that of hexaphenylethane. The compound absorbed oxygen, iodine, bromine, chlorine readily, i.e., it appeared to be unsaturated. Gomberg came to the conclusion that he had the free radical triphenylmethyl.

$$(C_6H_5)_3C\text{-}C(C_6H_5)_3 \rightleftharpoons 2(C_6H_5)_3C\cdot$$

Hexaphenylethane exists as such in the solid state but in solution dissociates into free radicals. The solution has a faint yellow

color, and in a short time the color reaches its maximum intensity indicating that equilibrium has been reached.

II. Properties

Free radicals are neutral molecules which, unlike ions, do not possess a charge. The dissociation of a hexaarylethane is a non-ionic process in which the pair of shared electrons between the ethane carbons are split, forming two particles, each with an unpaired electron.

$$R_3C:CR_3 \rightleftharpoons 2\ R_3C\cdot$$

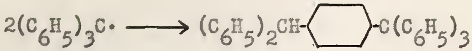
The presence of the odd electron gives the free radical characteristic properties.

(a) Peroxidation. Free radicals when allowed to stand in air are oxidized by the oxygen in the air to the peroxide.

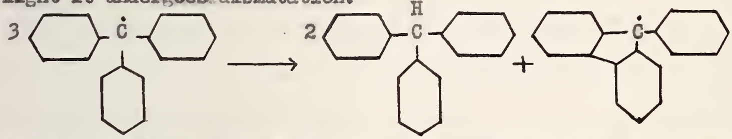
$$2\ R_3C\cdot + O_2 \longrightarrow R_3COOCR_3$$

The extent of oxidation depends upon the stability of the free radical. The peroxides are usually crystalline, stable compounds which may be isolated and used as a means of identifying the free radical.

(b) Dimerization. Another characteristic reaction of triarylmethyl radicals is the irreversible dimerization to an isomer of the hexaarylethane, e.g., a benzene solution of triphenylmethyl when treated with dry hydrogen chloride affords p-benzohydryltetraphenyl methane.



(c) Dismutation. Dismutation means that one molecule of the free radical becomes reduced at the expense of another molecule which becomes oxidized. When triphenylmethyl is exposed to sunlight it undergoes dismutation.



The 9-phenylfluorylmethyl, which is formed, associates completely at room temperature to give the corresponding hexaarylethane.

(d) Addition Reactions. Oxygen, chlorine, iodine, etc. are absorbed by a solution of free radicals.

$$2(C_6H_5)_3C\cdot + O_2 \longrightarrow (C_6H_5)_3COOC(C_6H_5)_3$$

$$2(C_6H_5)_3C\cdot + I_2 \rightleftharpoons 2(C_6H_5)_3CI$$

The absorption of iodine or oxygen can be used as a measure of the extent of dissociation of a hexaarylethane. Hydrogen is absorbed in the presence of platinum black.

$$2(C_6H_5)_3C\cdot + H_2(Pt) \longrightarrow 2(C_6H_5)_3CH$$

Sodium, as sodium amalgam, adds on to give the intensely red triphenylmethylsodium.

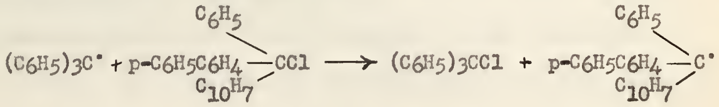
$$(C_6H_5)_3C^{\cdot} + Na \longrightarrow (C_6H_5)_3CNa$$

(e) Color. Free radicals are highly colored. This color has been attributed by Gomberg to the presence of a quinoid form of the free radical which is in equilibrium with the benzenoid form.

(f) Magnetism. A triaarylmethyl radical contains an unpaired electron and consequently is paramagnetic. This is due to the spin of the unpaired electron. Therefore, free radicals can be defined as compounds which possess magnetically non-compensated electrons. This also serves as a basis for the determination of the degree of dissociation of hexaarylethanes.

(g) Amphoterism. Triarylmethyls may be classified as amphoteric in that the triarylcarbinols react with mineral acids to give ionizable halochromic salts. The triarylmethanes react with sodium to give triarylmethylsodiums which yield triarylmethyl anions.

(h) The triarylmethyls possess a number of properties which find their counterpart in the behavior of metals. Just as one metal can displace another from a solution of its salt, so can one triarylmethyl displace another from its halide, e.g., addition of a yellow solution of triphenylmethyl to a colorless solution of phenyl-p-biphenyl-αnaphthylchloromethane evokes the deep brown color of phenyl-p-biphenyl-αnaphthylmethyl.



$$(C_6H_5)_3C^{\cdot} + p\text{-}C_6H_5C_6H_4-\overset{C_6H_5}{\underset{C_{10}H_7}{C}}Cl \longrightarrow (C_6H_5)_3CCl + p\text{-}C_6H_5C_6H_4-\overset{C_6H_5}{\underset{C_{10}H_7}{C}}{}^{\cdot}$$

Solutions of triarylmethyl radicals in liquid sulfur dioxide are

good conductors of electricity. The mechanism involved is that the triarylmethyl radical gives up its odd electron to the sulfur dioxide forming a cation.

$$(C_6H_5)_3C\cdot \longrightarrow (C_6H_5)_3C^{+} + e$$

This exchange enables the electricity to be carried through the solution.

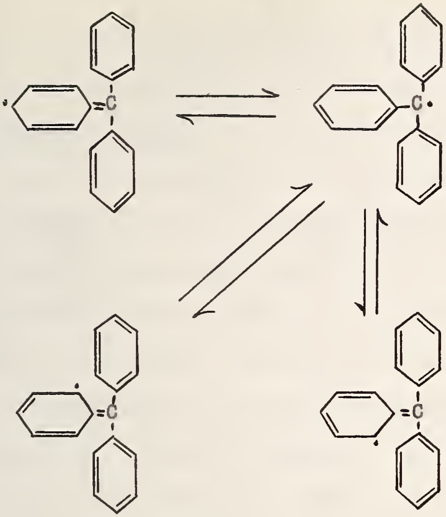
III. Stability of Free Radicals.

Several theories have been put forward to account for the stability of free radicals.

(a) Kharasch (3) considered that the electronegativities of the groups were of paramount importance in causing dissociation. According to this theory, the substitution of the hydrogens of ethane by more electronegative groups would result in the displacement of the valence electrons away from the central carbon atom, thus making the radical weakly electronegative. It was considered that two such weakly electronegative radicals would not form a stable compound. Therefore, the greater the electronegativity of a group, the greater the dissociation of the substituted ethane.

(b) Resonance. Pauling and Wheland (4) put forward the idea that dissociation is not due to a weakening of the carbon-carbon ethane linkage but rather to the stabilization of the free radicals through resonance. Triphenylmethyl may be used as an example.

The unpaired electron in triphenylmethyl can be smeared over each benzene ring in turn.



There are two ortho-positions and one para-position in each benzene ring to where the odd electron can move. Counting the three benzene rings we have nine resonating forms. If the resonating double bonds are taken into account there are a total of forty-four different forms. The number of resonating forms for the triphenylmethyl group in the hexaphenylethane is less than forty-four. So the formation of triphenylmethyl is favored due to its greater stability through resonance. If in place of a phenyl group we put another group like p-biphenyl or α-naphthyl, the number of resonating forms (involving a shift of the odd electron) will be increased and the free radical will be more stable than the corresponding hexaarylethane. However, there are certain groups which increase the

stability of a free radical, but not because of increased resonance. This may be explained by steric hindrance.

(c) Steric Hindrance. In hexaphenylethane each of the hydrogens of ethane have been replaced by a phenyl group. The steric hindrance arising from these six phenyl groups is sufficient to prevent a normal carbon-carbon bond from being formed, and to promote dissociation into free radicals. Tetraphenylethane, on the other hand, is quite stable. The steric hindrance here is not so great. Pentaphenylethane would occupy an intermediate position with regard to its tendency to dissociate into free radicals.

All of these factors, viz: resonance, steric hindrance and electronegativity must be taken into account when discussing the stability of free radicals. Recently, the ideas of resonance and steric hindrance have been prominent with regard to the stability of free radicals.

IV. Pentaarylethanes.

Up to this point the discussion of free radicals has dealt with hexaarylethanes only. Also important are the pentaarylethanes, about which this thesis is concerned.

The pentaarylethanes are colorless solids which give colorless solutions at room temperature (5). However, when the solution is heated to 80 - 100° a yellow color appears, indicating that dissociation has taken place at that elevated temperature into free radicals. Thus, with regard to stability, the pentaarylethanes occupy an intermediate position with respect to hexaaryl-

ethanes and tetraarylethanes. At 100° pentaarylethanes will absorb oxygen, bromine, iodine, etc. rapidly, indicating that dissociation has taken place and it is the free radical which is present in solution.

The increase in stability of pentaphenylethane over that of hexaphenylethane may be due to the loss of one benzene ring. This would decrease the steric effect and also cut down on the number of resonating forms for the free radical, thus stabilizing the pentaphenylethane.

From a study of the rate of oxygen absorption at 80 - 100° it was established that pentaphenylethane in solution undergoes dissociation into diphenylmethyl and triphenylmethyl radicals (6).

$$(C_6H_5)_3C\text{-}CH(C_6H_5)_2 \longrightarrow (C_6H_5)_3C\cdot + \cdot CH(C_6H_5)_2$$

Even in a colorless solution of pentaphenylethane this equilibrium exists. There is a rapid dissociation into free radicals which recombine, as quickly as they are formed, into pentaphenylethane.

The treatment of pentaarylethanes with oxygen at 80 - 100° results in the formation of the unsymmetrical peroxides. This oxidation process was shown by Bachmann and Wiselogle (6) to be a measure of the degree of dissociation of the pentaarylethane, i.e., the oxidation involves first the slow dissociation of the pentaarylethane into its free radicals and then the very rapid reaction of oxygen with the latter. Thus we have a first order, unimolecular reaction for the oxidation process.

Therefore: $\frac{dx}{dt} = k(a - x)$ where dx/dt = rate of reaction.
k = first order velocity constant.
$(a - x)$ = concentration of pentaphenylethane at time t.

Integrating: $k = \frac{2.3}{t} \log(\frac{a}{a - x})$

$= \frac{-2.3}{t} \log(1 - Z)$ where $Z = \frac{x}{a}$

= fraction of pentaphenylethane reacted at time t.

The value for Z may be taken as the ratio of the amount of oxygen absorbed at time t to the theoretical amount absorbed by all of the pentaarylethane. So by plotting t against $-\log(1 - Z)$, drawing the best-fitting straight line and calculating its slope, the value for k can be determined. Then the "half-life" period can be calculated ($t_{\frac{1}{2}} = \frac{2.3}{k} \log 2$).

Bachmann and Wiselogle (6) adopted the above procedure for determining the "half-life" periods of some pentaarylethanes.

It then became apparent that if the dissociation process was slow why could not another reaction, in place of oxidation, be used to determine the rate of dissociation. The reaction of iodine with free radicals is fast, just as the reaction of oxygen is with free radicals. Bachmann and Osborne (7) developed a new method for determining the rate of dissociation. Instead of with oxygen they allowed the pentaarylethanes to react with iodine.

The iodine was used in a solution of pyridine, o-dichloro-

benzene and ethanol. The o-dichlorobenzene acted as the inert solvent. The ethanol (absolute) served to convert the triphenylmethyl iodide to triphenylmethyl ethyl ether as fast as it was formed. This was necessary since the reaction of triphenylmethyl and iodine to give triphenylmethyl iodide is reversible. The pyridine was present to tie up with the hydrogen iodide (produced in the triphenylmethyl ethyl ether formation) in order to prevent it from reacting with the free radicals. The diphenylmethyl iodide tied up with the pyridine to give a quaternary salt in preference to forming an ether by reaction with the ethanol. The following reactions are those involved in this iodine method:

$$(C_6H_5)_3C\text{-}CH(C_6H_5)_2 \longrightarrow (C_6H_5)_3C\cdot + (C_6H_5)_2CH\cdot$$

$$2(C_6H_5)_3C\cdot + I_2 \longrightarrow 2(C_6H_5)_3CI$$

$$(C_6H_5)_3CI + C_2H_5OH \longrightarrow (C_6H_5)_3COC_2H_5 + HI$$

$$C_5H_5N + HI \longrightarrow C_5H_5NHI$$

$$2(C_6H_5)_2HC\cdot + I_2 \longrightarrow 2(C_6H_5)_2HCI$$

$$(C_6H_5)_2HCI + C_5H_5N \longrightarrow C_5H_5N\begin{cases} I \\ CH(C_6H_5)_2 \end{cases}$$

By this procedure Bachmann and Osborn (7) found that the dissociation of pentaarylethanes into free radicals was again the rate-controlling process, being first order and unimolecular.

Therefore, the following formula applied:

$$k = \frac{-2.3}{t} \log(1 - Z)$$

Where Z = fraction of pentaarylethane dissociated.

= ratio of iodine absorbed at time t to the theoretical absorption of iodine by all of the pentaarylethane.

The values obtained for the "half-life" periods by the iodine reaction checked with the values obtained by the oxygen reaction. Thus an easier method for determining rates of dissociation of pentaarylethanes was developed.

Using this method these workers proceeded to find out just what effect the replacing of phenyl groups by other groups had on the formation of free radicals from the pentaarylethanes. They tried the effect of a large number of groups and came to the conclusion that the groups could be arranged in order of their effectiveness in producing free radicals from the pentaarylethanes. The following list is in order of decreasing effectiveness: 9-phenanthyl, α-naphthyl, 2-fluoryl, p-biphenyl, p-anisyl, p-tolyl, phenyl.

Bachmann, Hoffman and Whitehead (8) prepared eighteen new pentaarylethanes and thus obtained a more complete picture on the effect of various groups. Four phenyl groups and one aryl group were present in each of the pentaarylethanes.

The work outlined in this thesis has to do with the preparation and determination of "half-life" periods of four more pentaarylethanes. The effectiveness of the different substituent

groups in promoting dissociation of pentaarylethanes into free radicals can be compared with the results in the last report by Bachmann and his co-workers (8).

Discussion

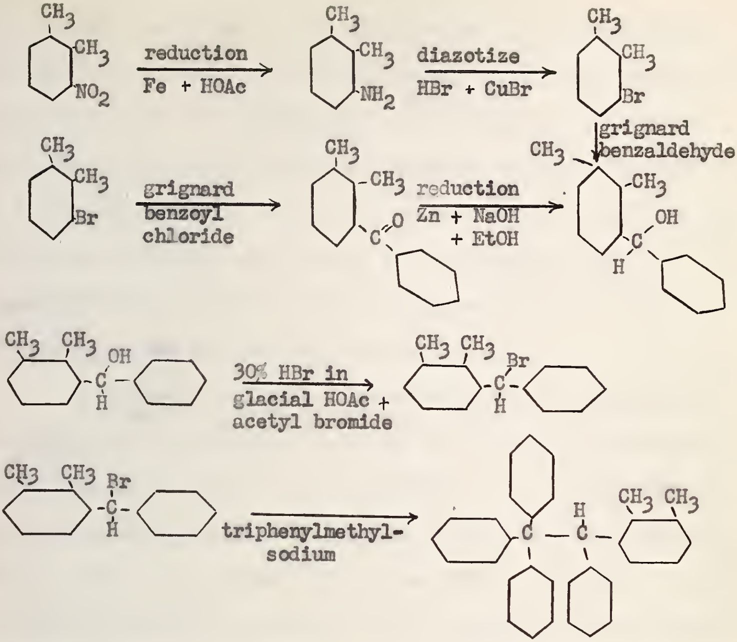
It was decided to test some of the data put forward by Bachmann and his co-workers (6)(7)(8). If check results could be obtained our technique would be good enough to give meaning to the "half-life" periods of the four compounds synthesized. The compound chosen was pentaphenylethane.

I. Synthesis of Pentaphenylethane.

The method used by Bachmann (5) was also used here. Triphenylcarbinol was prepared by the action of two moles of bromobenzene and magnesium on one mole of ethylbenzoate. This was converted to triphenylbromomethane by the action of acetyl bromide. Benzophenone was reduced to benzhydrol using zinc, sodium hydroxide and 95% ethanol. The benzhydrol was converted to diphenylbromomethane by the action of a 30% solution of hydrogen bromide in glacial acetic acid, and acetyl bromide. Then the triphenylbromomethane was converted to the triphenylmethylmagnesium bromide and allowed to react with diphenylbromomethane. The result was a 72% yield of white platelets of pentaphenylethane, melting at 165 - 178° with decomposition.

II. Synthesis of 1,1,1,2-Tetraphenyl-2(3-o-xylyl)ethane.

A review of the literature revealed that this compound had not been synthesized previously. The following series of reactions was decided upon to prepare the compound:



The reduction of 3-o-nitroxylene using iron and 5% acetic acid worked very nicely giving a good yield of 3-o-xylidine. Then just to make certain that there was no 4-o-xylidine present (as an impurity), the 3-o-xylidine was converted to the formyl derivative and purified by recrystallization. The formyl derivative was hydrolized and the pure 3-o-xylidine recovered with very little loss.

The 3-o-xylidine was diazotized with 48% hydrobromic acid and then allowed to react with the cuprous bromide in the cold. The resulting 3-o-bromoxylene was obtained in very poor yields (27%) (9).

At this point there were two possibilities for preparing

2,3-dimethylbenzhydrol. By the first method 3-o-bromoxylene was converted to the grignard using magnesium, and this was allowed to react with freshly vacuum-distilled benzaldehyde. This reaction gave very poor yields, and in some cases did not yield any carbinol. However, when the reaction was carried out at lowered temperatures and hydrolysis was affected by a saturated solution of ammonium chloride and ice, instead of hydrochloric acid and ice, 44% yields of the carbinol were obtained.

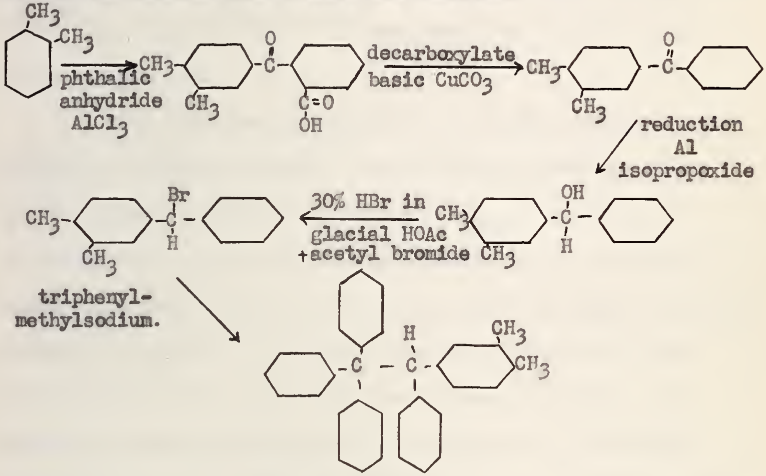
By the second method, 3-o-bromoxylene was converted to the grignard using magnesium and this was allowed to react with freshly vacuum-distilled benzoyl chloride. The resulting ketone, 2,3-dimethylbenzophenone, was obtained in only 45% yield. It was reduced using zinc, sodium hydroxide and 95% ethanol.(10). The 2,3-dimethylbenzhydrol obtained by this procedure was of the same quality as that prepared by the benzaldehyde reaction.

The carbinol was converted to 3-o-xylylphenylmethyl bromide through the action of 30% hydrogen bromide in glacial acetic acid, and acetyl bromide, according to the procedure of Bachmann (5). The bromo-compound, on being purified by vacuum-distillation, was allowed to react with triphenylmethylsodium (6). Some difficulty was encountered in the recrystallizing of the pentaarylethane. This was found to be due to the chloroform-ethanol mixture used in the recrystallization. When a benzene-ethanol mixture was used the pure 1,1,1,2-tetraphenyl-2(3-o-xylyl)ethane was easily obtained. After drying in vacuo at 100° until a good check with carbon and

hydrogen analysis was obtained, the "half-life" period was determined according to the procedure used by Bachmann and his co-workers (7)(8).

III. Synthesis of 1,1,1,2-Tetraphenyl-2(4-o-xylyl)ethane.

A review of the literature revealed that this compound had not been synthesized previously. The following series of reactions was decided upon to make the compound:



At first an attempt was made to prepare 4-o-bromoxylene. This could have been converted to the grignard and then by reaction with benzoyl chloride to the 3,4-dimethylbenzophenone.

Jacobsen (11) stated that 4-o-bromoxylene could be prepared by the direct bromination of o-xylene. This reaction did work well but there was some doubt as to whether or not some of the 3-o-bromoxylene was present.

Barnett and Marrison (12) stated that o-3,4-dimethylbenzoylbenzoic acid could be prepared free from its isomer (o-2,3-dimethylbenzoylbenzoic acid). So, o-xylene was allowed to react with phthalic anhydride and aluminum chloride in nitrobenzene. The resulting keto-carboxylic acid had a sharp melting point, 163 - 165°. The above reference gave a melting point of 167°. The keto-carboxylic acid was decarboxylated using basic copper carbonate (13). As a result 3,4-dimethylbenzophenone was prepared, and melted at 40 - 43°.

Elbs (14) treated o-xylene with benzoyl chloride in the presence of aluminum chloride. The resulting colorless, thick liquid, which solidified in a few days (m.p., 47 - 48°), was claimed by Elbs to be the 3,4-dimethylbenzophenone. He gave no experimental proof but came to this conclusion by saying that this reaction was similar to the ones where phthalic anhydride and acetyl chloride were used in place of benzoyl chloride. The structure of the keto-carboxylic acid and of the 3,4-dimethylacetophenone had been proven so Elbs came to the conclusion that he had the 3,4-dimethylbenzophenone. There was still some doubt about this, therefore, the method followed was to use phthalic anhydride with o-xylene and decarboxylate the resulting acid.

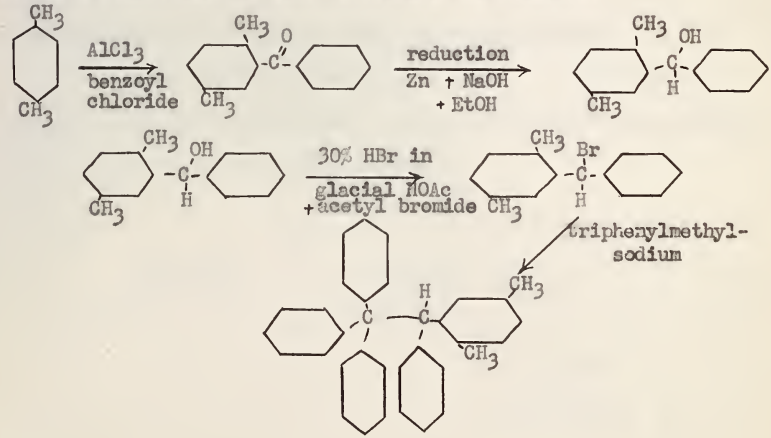
Various attempts were made to reduce this ketone to the 3,4-dimethylbenzhydrol. The use of zinc dust, sodium hydroxide and 95% ethanol (10) proved to be unsuccessful. A second attempt at reduction involved the use of a 2% sodium amalgam and ethanol

(15). This also proved to be useless. As a last resort aluminum isopropoxide was used as the reducing agent (16)(17). This reaction worked well, and as a result 3,4-dimethylbenzhydrol was prepared in 90% yields. It crystallized out by itself and had an m.p. = 48 - 58°.

The remainder of the synthesis of this pentaarylethane is analogous to the synthesis of 1,1,1,2-tetraphenyl-2(3-o-xylyl)-ethane, i.e., the 3,4-dimethylbenzhydrol was converted to the bromide through the action of 30% hydrogen bromide in glacial acetic acid, and acetyl bromide (5). The 4-o-xylylphenylbromomethane was converted to the pentaarylethane by reacting with triphenylmethylsodium (6).

IV. Synthesis of 1,1,1,2-tetraphenyl-2(2-p-xylyl)ethane.

Further review of the literature revealed that this pentaarylethans had not as yet been synthesized. The following series of reactions was used to prepare the compound.



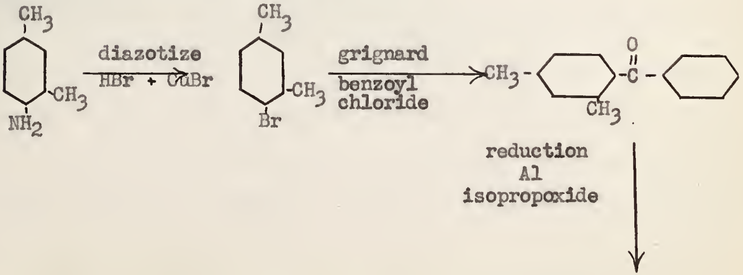
Elbs (14) first prepared 2,5-dimethylbenzophenone by the action of benzoyl chloride on p-xylene in the presence of aluminum chloride. Since there was no possibility of isomer formation by this reaction, p-xylene was allowed to react with benzoyl chloride in carbon disulfide with aluminum chloride present. The resulting ketone had a sharp boiling point but did not solidify.

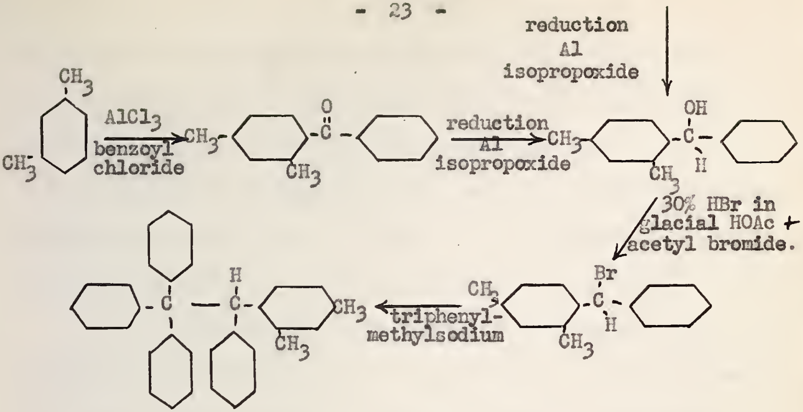
By treatment of the ketone with zinc dust, sodium hydroxide and 95% ethanol (10) the 2,5-dimethylbenzhydrol was prepared. It was obtained as a white solid melting at 85 - 86°. This checked very well with Elbs (14) who gave an m.p. = 88° by repeated recrystallizations.

The remainder of the synthesis of this pentaarylethane is analogous to the synthesis of the first two. The carbinol was converted to the 2-p-xylylphenylbromomethane (5) and this was allowed to react with triphenylmethylsodium (6) to give the required pentaarylethane.

V. Synthesis of 1,1,1,2-tetraphenyl-2(4-m-xylyl)ethane.

A review of the literature revealed that this compound had not as yet been synthesized. The following series of reactions was used to prepare the pentaarylethane:





The first attempt at preparing this pentaarylethane started with 4-m-xylidine. This compound was changed into 4-m-bromoxylene by first diazotizing with 48% hydrobromic acid and then treating with cuprous bromide in the cold (9). Again the yields were very poor. The 4-m-bromoxylene was converted to the grignard using magnesium and then allowed to react with benzoyl chloride. The 2,4-dimethylbenzophenone was obtained in only 40% yield. An attempt was then made to reduce the ketone to 2,4-dimethylbenzhydrol using zinc dust, sodium hydroxide and 95% ethanol (10). No carbinol was obtained so this method was abandoned.

Elbs (14) prepared 2,4-dimethylbenzophenone through the action of benzoyl chloride on m-xylene in the presence of aluminum chloride. However, he was not able to prove its structure. Instead he assumed that the ketone was 2,4-dimethylbenzophenone by analogous reactions of phthalic anhydride and acetyl chloride with

m-xylene. The keto-carboxylic acid and the 2,4-dimethylacetophenone had their structures proven. Therefore he came to the conclusion that he had the 2,4-dimethylbenzophenone.

m-Xylene was allowed to react with freshly vacuum-distilled benzoylchloride in carbon disulfide in the presence of aluminum chloride. The resulting ketone was obtained in good yield.

The 2,4-dimethylbenzophenone was reduced to the 2,4-dimethylbenzhydrol using aluminum isopropoxide as a reducing agent (16). This reaction worked well and as a result 3,4-dimethylbenzhydrol was obtained in 87% yield. The carbinol, according to Elbs (14) was difficult to crystallize. Finally he was able to obtain a solid which melted at 57°. This reaction yielded an oil which did not solidify but only became opaque and viscous.

The remainder of the synthesis of this pentaarylethane is analogous to the synthesis of 1,1,1,2-tetraphenyl-2(3-o-xylyl)ethane, i.e., the 2,4-dimethylbenzhydrol was converted to the bromide through the action of 30% hydrogen bromide in glacial acetic acid, and acetyl bromide (5). The 4-m-xylylphenylbromomethane was converted to the pentaarylethane by reacting with triphenylmethylsodium (6).

Once the pentaarylethanes were synthesized, their "half-life" periods were determined using the method of Bachmann and Osborne (7).

Pentaphenylethane was used, to test the data put forward by Bachmann and his co-workers (7)(8), and also to become acquaint-

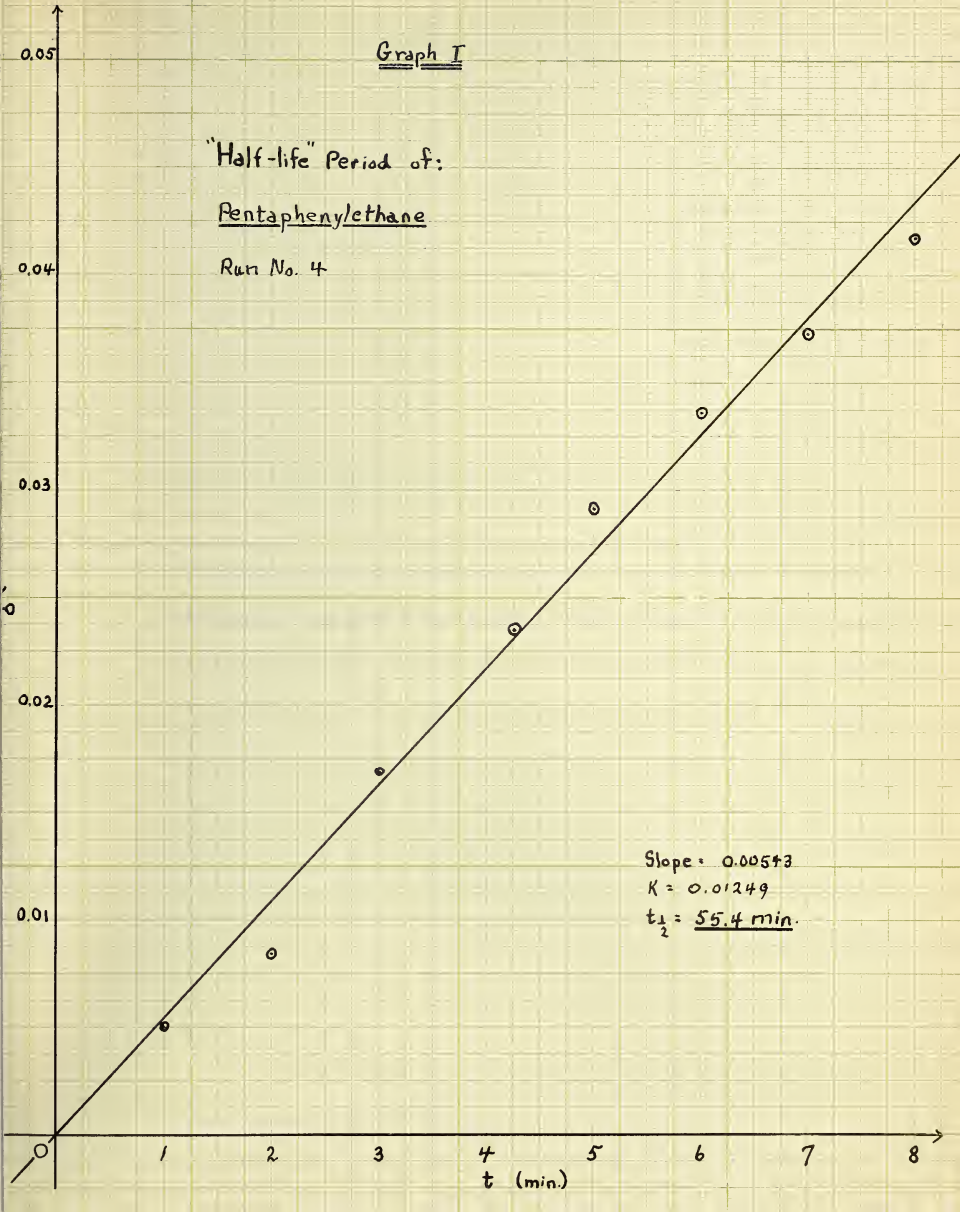
ed with the procedure employed. Five determinations were made and the following "half-life" periods were obtained (Table 1).

Run No.	"Half-life" Period (min.)
1	58.7
2	48.4
3	53.1
4	55.4
5	56.4

Table 1 - "Half-life" period, pentaphenylethane.

The first three runs were considerably different from the value obtained by Bachmann (56.0 min.). However, as the technique improved, the results obtained checked very well with that of Bachmann. Run 4 is shown on Graph I, with a "half-life" period of 55.4 minutes.

1,1,1,2-Tetraphenyl-2(3-o-xylyl)ethane was the next pentaarylethane examined. Eight runs were carried out and the "half-life" periods are shown in Table 2. In runs 1, 2 and 3 the reaction period went up to ten minutes. Two lines were obtained in run 2 with the same slope but displaced from each other. In run 3 two lines were obtained with different slopes. The first few points gave a line with a steeper slope, and therefore a shorter "half-life" period, than the last few points. Bachmann and Osborne (7) determined the "half-life" period of pentaphenylethane at various temperatures. At 94.9° they obtained a "half-life" period of 11.4 minutes. From their graph it was seen that the reaction lasted only six minutes. Therefore, it was decided to keep the reaction



Graph I

"Half-life" Period of:

Pentaphenylethane

Run No. 4

Slope = 0.00543

$K = 0.01249$

$t_{\frac{1}{2}} = $ 55.4 min.

Run No.	"Half-life" Period (min.)	
1	14.3	
2	13.1	13.1
3	12.8	15.1
4	13.1	
5	18.2	
6	14.3	
7	16.4	
8	15.3	

Table 2 - "Half-life" period 1,1,1,2-tetraphenyl-2(3-o-xylyl)ethane.

period for 1,1,1,2-tetraphenyl-2(3-o-xylyl)-ethane down to five minutes, since its "half-life" period was quite short. In run 4 the reaction period lasted up to five minutes and a straight line was the result. In run 5 the samples were allowed to react for periods of time varying from six to ten minutes. From these results the conclusion was drawn that the reaction should be allowed to run for only five minutes. A new batch of the pentaarylethane was prepared, but the carbon content was 1% too low. Run 6 gave a high result with this batch. By recrystallization the carbon content was 3% too low, and the "half-life" period (run 7) was still higher. In run 8 the same batch of pentaarylethane had been dried for a long time and the carbon content brought up so that it was only 0.6% low. The value obtained was again high. Before drawing conclusions from these values, some more of the pentaarylethane was prepared with care.

In the meantime, "half-life" periods were run on the three other pentaarylethanes.

Less difficulty was encountered in the determination of the "half-life" period of 1,1,1,2-tetraphenyl-2(4-o-xylyl)ethane. Four runs were made, the "half-life" periods of which are shown in Table 3.

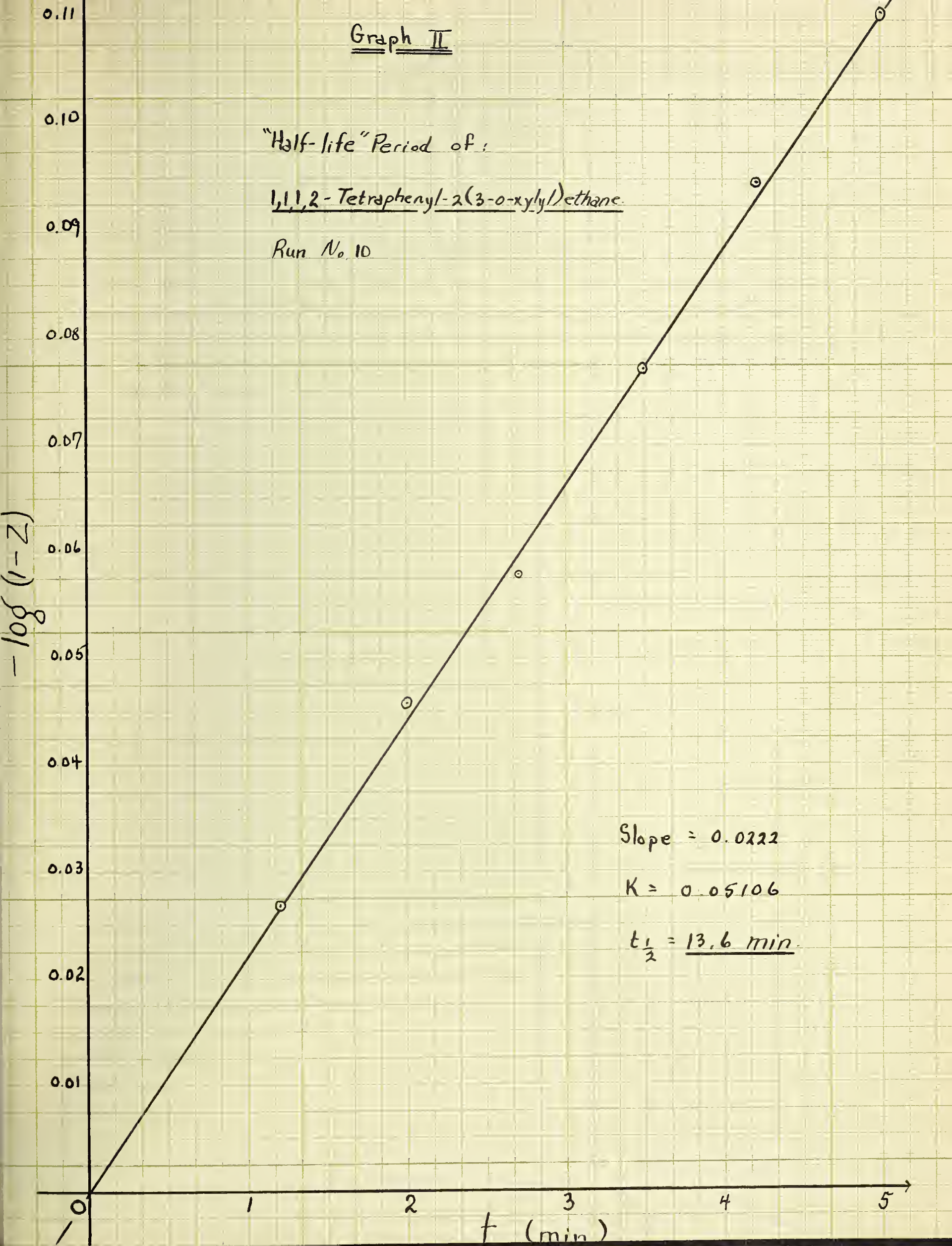
Run No.	"Half-life" Period (min.)
1	46.5
2	49.6
3	47.6
4	46.9

Table 3 - "Half-life" period, 1,1,1,2-tetraphenyl-2(4-o-xylyl)ethane

In runs 1,2 and 3 the reaction period went up to five minutes, while in the last run it went up to ten minutes. The value obtained in run 2 (49.6 min.) can be disregarded. A very erratic graph was obtained, due probably to the fact that the temperature control broke down and the temperature varied considerably. The values obtained in runs 1, 3 and 4 checked very nicely. Run 4 is shown on graph III. The average of runs 1, 3 and 4 was taken as the final value for the "half-life" period.

The "half-life" period of 1,1,1,2-tetraphenyl-2(2-p-xylyl)-ethane was obtained by making two runs. The values were 15.1 min. and 15.7 min. Because the "half-life" periods were so short the reaction period went up to only five minutes. The first run is shown on Graph IV. The average of the first and second runs was taken as the final value for the "half-life" period.

The "half-life" period of 1,1,1,2-tetraphenyl-2(4-m-xylyl)-ethane was also obtained with comparative ease. The first two runs



Graph II

"Half-life" Period of:

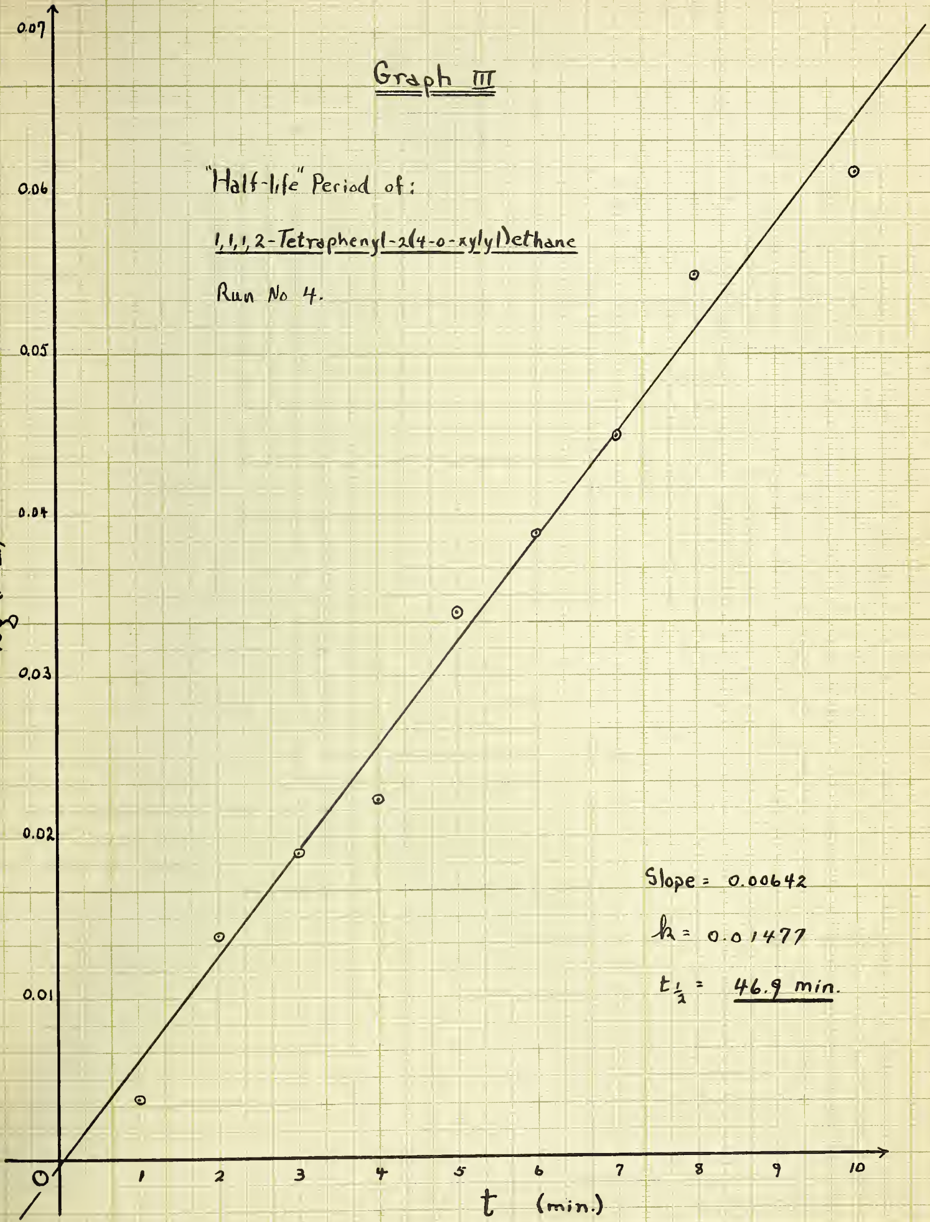
1,1,1,2-Tetraphenyl-2(3-o-xylyl)ethane

Run No. 10

Slope = 0.0222

K = 0.05106

$t_{\frac{1}{2}}$ = 13.6 min



Graph III

"Half-life" Period of:

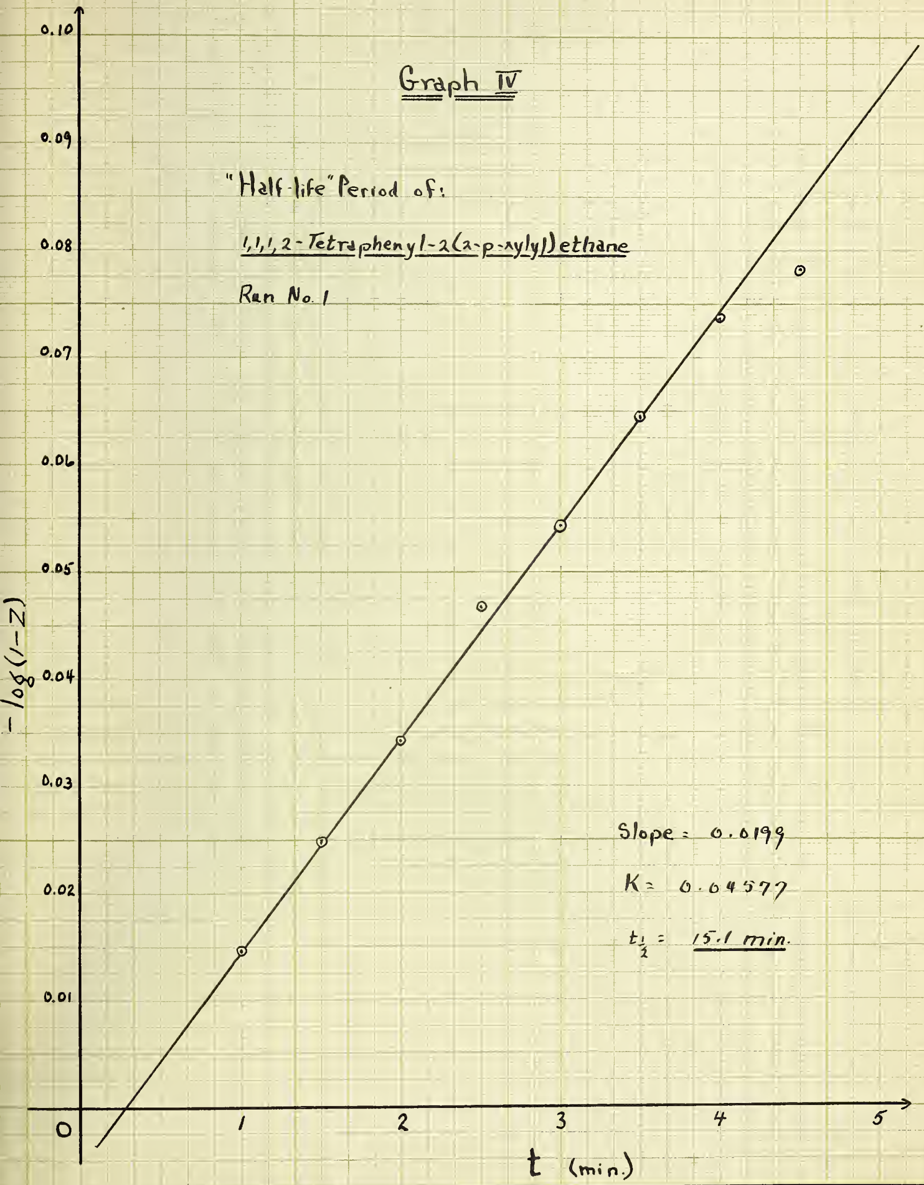
1,1,1,2-Tetraphenyl-2(4-o-xylyl)ethane

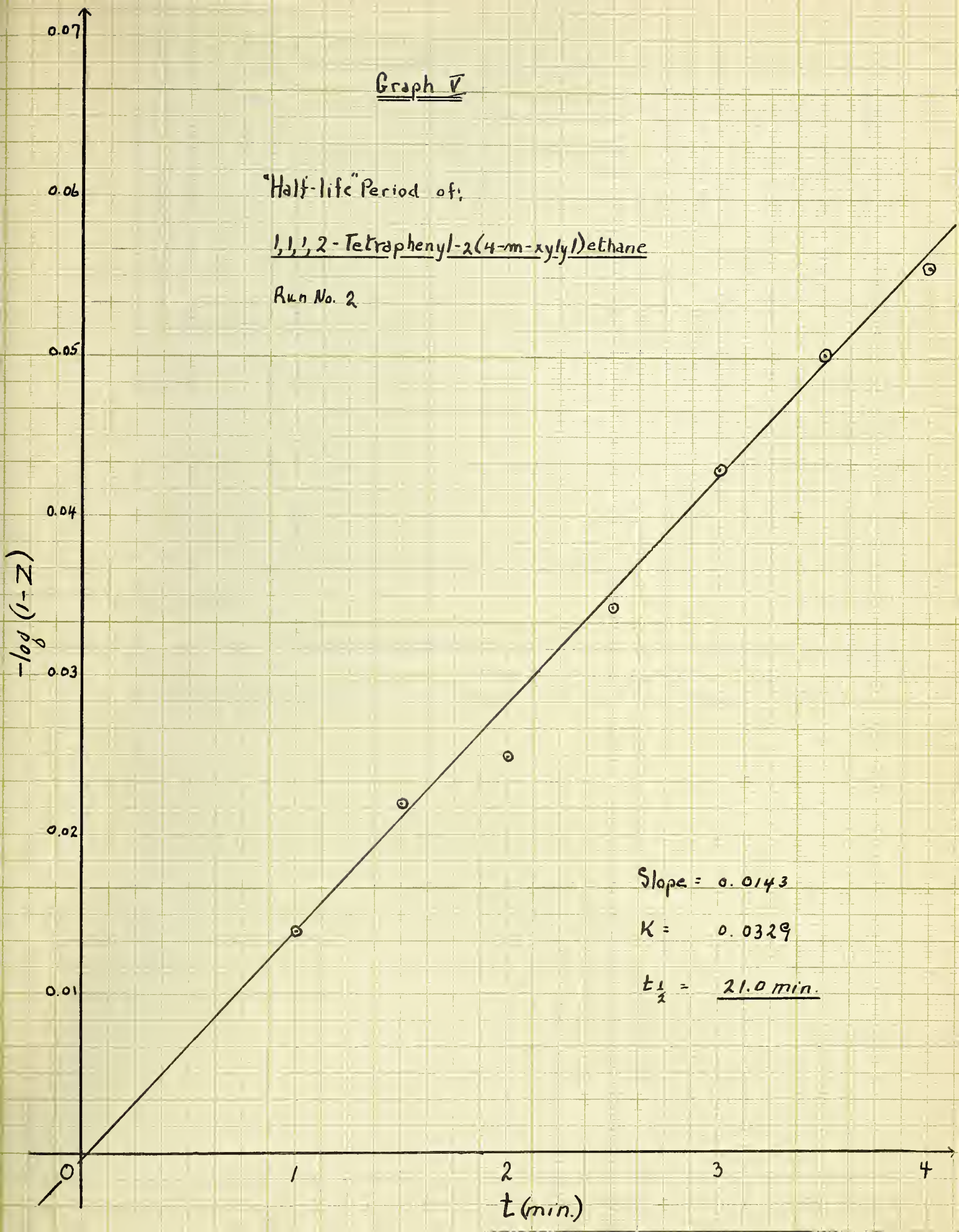
Run No 4.

Slope = 0.00642

k = 0.01477

$t_{\frac{1}{2}}$ = **46.9 min.**


Graph IV
"Half-life" Period of:
1,1,1,2-Tetraphenyl-2(2-p-xylyl)ethane
Run No. 1
Slope = 0.0199
K = 0.04577
$t_{\frac{1}{2}}$ = 15.1 min.
$-\log_{10}(1-Z)$
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
1
2
3
4
5
t (min.)



Graph V

"Half-life" Period of:

1,1,1,2-Tetraphenyl-2(4-m-xylyl)ethane

Run No. 2

Slope = 0.0143

K = 0.0329

$t_{\frac{1}{2}}$ = 21.0 min.

gave results which checked within the 5% experimental error of Bachmann. The values obtained were 20.4 min. and 21.0 min. The average of the two was taken as the final value for the "half-life" period. The curve obtained in the second run is shown in Graph V.

Some more 1,1,1,2-tetraphenyl-2(3-o-xylyl)ethane, which was very pure according to a carbon-hydrogen analysis, was prepared. Two determinations were made with the following results: run 9, 13.4 min.; run 10, 13.6 min. Graph II shows the curve obtained in run 10. These two values checked very well with each other and also with the value obtained in run 4 (13.1 min.). The average of runs 4, 9 and 10 was taken as the final value for the "half-life" period.

The pentaarylethanes and their rate constants (average) and their "half-life" periods (average) are shown in Table 4.

Table 4

Rate Constants and "Half-life" periods of 1,1,1,2-Tetraphenyl-2-arylethanes

(Arranged in order of decreasing rate of dissociation)

$(C_6H_5)_3C-CH(C_6H_5)R$

Temp., 80°.

Aryl Group R	Rate Constant k	"Half-life"Period $t_{\frac{1}{2}}$ (min.)
3-o-xylyl	0.0517	13.4
2-p-xylyl	0.0450	15.4
4-m-xylyl	0.0334	20.7
4-o-xylyl	0.0147	47.0
phenyl (a)	0.0124	56.0

(a) Determined by Bachmann and Osborne (7).

From the results in Table 4 it was seen that the shifting of the two methyl groups to different locations on the one benzene ring resulted in varying degrees of influence on reactions involving the methane carbon atom.

The short "half-life" period of 1,1,1,2-tetraphenyl-2-(3-o-xylyl)ethane (II) substantiated the extreme reactivity of 1,2,9,10-tetramethylanthracene (I).

Experimental Procedure

All melting points and boiling points, unless otherwise indicated, were uncorrected. Carbon-hydrogen analyses were performed by J. C. Nichol using the semi-micro apparatus of Niederl and Niederl (18).

I. Pentaphenylethane.

The procedure followed for the synthesis of pentaphenylethane was the same as that used by Bachmann (5). The pentaphenylethane was obtained in colorless plates by recrystallization from a chloroform-ethanol mixture; m.p., 165 - 178° dec. in air; yield, 70%.

II. 1,1,1,2-Tetraphenyl-2(3-o-xylyl)ethane.

(a) 3-o-Xylidine (19).

3-o-Nitroxylene (80 g.) was added, 5 cc. at a time, with constant shaking to 200 g. of iron and 325 cc. of 5% acetic acid contained in a 2 liter flask fitted with an air condensor. This mixture was heated on a water-bath for three hours, made alkaline with sodium hydroxide and steam-distilled. The distillate was extracted with benzene and dried over sodium sulfate. The benzene was removed by distillation and the 3-o-xylidine obtained as a clear, orange-colored oil boiling at 223°; yield, 80%.

(b) Purification of 3-o-Xylidine (9).

3-o-Xylidine (75 g.), 35 cc. of formic acid and 125 cc. of water was heated on a water-bath for four hours. On cooling,

the formyl derivative solidified. It was filtered by suction and washed well with water. It was purified by recrystallization from ethanol and then hydrolized with an alcoholic potassium hydroxide solution. The ethanol was distilled over and the 3-o-xylidine obtained free of base by steam distillation. The distillate was extracted with benzene. The 3-o-xylidine was distilled at 215 - 221° (686 mm.).

(c) 3-o-Bromoxylene.

The hydrobromic acid salt of 3-o-xylidine was prepared by heating 22 g. of 3-o-xylidine, 50 cc. of water and 100 cc. of 48% hydrobromic acid until all was in solution. This was cooled quickly with stirring to 0 - 5°. Sodium nitrite (13.5 g.) in 25 cc. of water was added slowly, keeping the temperature below 5°.

Copper turnings (5.8 g.), cupric bromide (20.3 g.), 48% hydrobromic acid (75 cc.) and 200 cc. of water had been refluxed until the solution was almost colorless or only a faint yellow (5 hours).

The cuprous bromide solution was cooled to 0 - 5° and the above diazonium salt added. The mixture was kept in an ice-bath for fifteen minutes, at room temperature for two hours and in hot water for thirty minutes. When the red precipitate had become oily and had sunk to the bottom, the mixture was steam-distilled. The distillate was made alkaline with sodium hydroxide and steam distilled again. The final distillate was extracted with benzene which was then dried over sodium sulfate. The 3-o-

bromoxylene (27% yield) boiled at 211 - 215°.

(d) 2,3-Dimethylbenzhydrol.

3-o-Bromoxylene (10 g.), 1.5 g. of magnesium, 10 cc. of ether and 10 cc. of benzene was placed in a tightly stoppered flask with a crystal of iodine to initiate the reaction. The reaction was allowed to proceed at room temperature for two to three days. The grignard solution was then decanted from the excess magnesium, 5 cc. of benzaldehyde was added to the cold solution and washed in with 25 cc. of ether.

At this point three such solutions, after sitting overnight at room temperature in tightly stoppered flasks, were combined. Hydrolysis was affected with a saturated solution of ammonium chloride in ice and water. The benzene layer was washed with saturated solutions of sodium bisulfite, sodium bicarbonate and finally with water, and then dried over sodium sulfate. The solvents were removed by distillation at atmospheric pressure. The carbinol was obtained as a lemon yellow oil boiling at 161 - 166° (2 mm.); yield, 44%; m.p., 64 - 70°.

Anal. Calc'd. for $C_{15}H_{16}O$: C, 84.9; H, 7.6.
Found: C, 84.4; H, 7.9.

The benzaldehyde used was specially prepared. First, some ordinary benzaldehyde was shaken with a saturated solution of sodium bicarbonate until effervescence stopped. Then it was dried over sodium sulfate and finally vacuum-distilled, a middle fraction being collected. It was used directly after distillation.

(e) 3-o-Xylylphenylmethyl Bromide (5).

2,3-Dimethylbenzhydrol (10.5 g.) and 43 cc. of 30% hydrogen bromide in glacial acetic acid was heated on a water-bath for two hours. After cooling slightly, 8 cc. of acetyl bromide was added, and the mixture was heated two hours more on a water-bath. It was allowed to sit at room temperature overnight. The solvents were removed by distillation under reduced pressure and the bromide purified by distillation under reduced pressure; b.p., 158 - 164° (3 mm.); yield, 70%.

(f) 1,1,1,2-Tetraphenyl-2(3-o-xylyl)ethane (6).

To 45 g. of molten sodium under xylene in a 250-cc. Erlenmyer flask 55 g. of mercury was added slowly through a pin-point hole in a folded filter-paper. After the flask had cooled to room temperature the amalgam was pipetted out carefully and placed under 50 cc. of benzene and 50 cc. of ether in a glass-stoppered bottle.

To this amalgam in a 500 cc. glass-stoppered bottle was added 9 g. of triphenylchloromethane. The bottle was sealed with special stop-cock grease (20), cooled in an ice-bath and shaken by hand. The red color of triphenylmethylsodium appeared almost at once. The bottle was kept in an ice-bath for one to two hours and then allowed to stand at room temperature for one day. The sodium amalgam was frozen by immersing the bottle in an ice-salt bath and 9 g. of 3-o-xylylphenylmethyl bromide quickly added. The intense red color disappeared almost immediately. The solution was

decanted from the sodium amalgam and benzene used to wash the latter. The benzene layer was hydrolized with ice, water and hydrochloric acid, washed well with water and dried over sodium sulfate. To the dry benzene solution was added sufficient ethanol to cause the pentaarylethane to precipitate. The crystals were washed well with alcohol and dried in vacuo at 100° until a carbon-hydrogen analysis indicated no solvent of crystallization present. A 63% yield of white crystals of the pentaarylethane was obtained; m.p., 171 - 183° dec in air.

Anal. Calc'd. for $C_{34}H_{30}$: C, 93.09; H, 6.91.
Found: C, 92.92; H, 7.22.

III. 1,1,1,2-Tetraphenyl-2(4-o-xylyl)ethane.

(a) o-3,4-Dimethylbenzoylbenzoic Acid (12).

o-Xylene (50 g.), phthalic anhydride (64 g.) and nitrobenzene (300 cc.) was stirred for thirty minutes and then 157 g. of aluminum chloride was slowly added over a period of one and a half hours. The mixture was allowed to sit overnight at room temperature, and in the morning, heated on a water-bath at 60 - 65° for two hours. Hydrolysis was affected with two liters of ice and hydrochloric acid. The oily solid was washed by decantation, dissolved in sodium hydroxide solution and steam-distilled. The residue was cooled, acidified with hydrochloric acid and allowed to sit overnight. In some cases when a lot of tar was present the alkaline residue was extracted with benzene. The aqueous layer was then made acid and allowed to sit overnight in

the ice-box. The solid was recrystallized from ethanol; m.p., 161 - 164°; yield, 77%.

(b) 3,4-Dimethylbenzophenone (13).

o-3,4-Dimethylbenzoylbenzoic acid (49 g.) was heated with a free flame in a 125-cc. Claisen distilling-flask to 200° to eliminate all moisture. A thermometer was in the molten acid. The acid was cooled and 1 g. of basic copper carbonate was added. The mixture was heated rapidly to 265°, using a salt-bath, and kept at temperature until no more carbon dioxide was evolved. After fifteen minutes the heat was removed and the flask set up for a vacuum distillation. The 3,4-dimethylbenzophenone boiled at 165 - 168° (3 mm.); yield, 63%.

The basic copper carbonate was prepared in the following manner: sodium carbonate (17.6 g.) was mixed with an aqueous solution of 16 g. of copper sulfate, heated and then cooled. The green precipitate was filtered and air-dried.

(c) 3,4-Dimethylbenzhydrol (16).

Aluminum wire (2.4 g.) was refluxed with 100 cc. of isopropyl alcohol (distilled from sodium) until all the aluminum had gone into solution. A pinch of mercuric chloride was used as a catalyst. The isopropyl alcohol was distilled off. 3,4-Dimethylbenzophenone (13.5 g.) in 100 cc. of dry toluene was added and the mixture refluxed for four hours. Isopropyl alcohol (distilled from sodium) (50 cc.) was added and fractionally distilled over a period of one hour using a Snyder column. The fractional distill-

ation was repeated with another 50 cc. of isopropyl alcohol. The residue was hydrolized with ice and sulfuric acid and dried over sodium sulfate. The solvents were removed under reduced pressure. The 3,4-dimethylbenzhydrol boiled at 164 - 168° (2 mm.); yield, 90%; m.p., 48 - 58°.

(d) 4-o-Xylylphenylmethyl Bromide (5).

The procedure followed was the same as in the preparation of 3-o-xylylphenylmethyl bromide. The bromide was purified by distillation under reduced pressure; b.p., 187 - 188° (8 mm.); yield, 70%.

(e) 1,1,1,2-Tetraphenyl-2(4-o-xylyl)ethane (6).

The procedure followed was the same as for the preparation of 1,1,1,2-tetraphenyl-2(3-o-xylyl)ethane. Due to the greater solubility of this compound it was necessary to remove the benzene by distillation in vacuo and then to recrystallize from a benzene-methanol mixture. The compound was dried in vacuo at 100° until a carbon-hydrogen analysis indicated no solvent of crystallization present. A 60% yield of slightly yellow crystals of the pentaarylethane was obtained; m.p., 164 - 178° dec. in air.

Anal. Calc'd. for $C_{34}H_{30}$: C, 93.09; H, 6.91.

Found: C, 93.07; H, 7.00.

IV. 1,1,1,2-Tetraphenyl-2(2-p-xylyl)ethane.

(a) 2,5-Dimethylbenzophenone (21).

To 72 g. of p-xylene, 94 g. of freshly vacuum-distilled benzoyl chloride and 200 g. of carbon disulfide was added 100 g.

of finely powdered aluminum chloride over a period of one and a quarter hours. The mixture was allowed to sit overnight at room temperature, and in the morning was refluxed for five hours. Hydrolysis was affected by pouring the solution into 1 liter of ice and 200 cc. of concentrated hydrochloric acid. The carbon disulfide was removed by steam distillation and the residue extracted with benzene. The benzene solution was washed with sodium bicarbonate and water and dried over sodium sulfate. The benzene was distilled at atmospheric pressure. The 2,5-dimethylbenzophenone boiled at 161 - 164° (4 mm.); yield, 77%.

(b) 2,5-Dimethylbenzhydrol (10)(14).

2,5-Dimethylbenzophenone (110 g.), sodium hydroxide pellets (110 g.) and 95% ethanol (1100 cc.) was refluxed until the solution became dark brown in color (one hour). Zinc dust (110 g.) was added over a period of thirty minutes, and the mixture was refluxed until the solution was a faint yellow (two and a half hours). The mixture was cooled, the zinc dust removed by suction filtration and the filtrate poured into 3 liters of ice and water plus 300 cc. of concentrated hydrochloric acid. The precipitate was recrystallized from ethanol; yield, 96%; m.p., 85 - 86°.

(c) 2-p-Xylylphenylmethyl bromide (5).

The procedure followed was the same as in the preparation of 3-o-xylylphenylmethyl bromide. The bromide boiled at 187 - 189° (13 mm.); yield, 85%. It was used at once, without analysis for bromine, in the preparation of the pentaarylethane.

(d) 1,1,1,2-Tetraphenyl-2(2-p-xylyl)ethane (6).

The procedure followed was the same as for the preparation of 1,1,1,2-tetraphenyl-2(3-o-xylyl)ethane. This pentaarylethane was recrystallized from a benzene-ethanol mixture. After two recrystallizations a 50% yield was obtained. The crystals were dried in vacuo at 100° until a carbon-hydrogen analysis showed no solvent of crystallization to be present; m.p., 168 - 179° dec. in air.

Anal. Calc'd. for $C_{34}H_{30}$: C, 93.09; H, 6.91.

Found: C, 92.60; H, 7.10.

V. 1,1,1,2-Tetraphenyl-2(4-m-xylyl)ethane.

(a) 2,4-Dimethylbenzophenone (14).

To 84 g. of m-xylene, 77 cc. of benzoyl chloride and 150 cc. of carbon disulfide was added 100 g. of finely powdered aluminum chloride over a period of one hour. The mixture was allowed to stand overnight at room temperature and then refluxed for four and a half hours. Hydrolysis was affected by pouring the mixture into 1 liter of ice and hydrochloric acid. The carbon disulfide was removed by a steam distillation, and the residue extracted with benzene. The benzene solution was washed with sodium bicarbonate and water and dried over sodium sulfate. The benzene was distilled at atmospheric pressure. The 2,4-dimethylbenzophenone boiled at 150 - 152 °(2 mm.); yield, 89%.

(b) 2,4-Dimethylbenzhydrol (10)(14).

The procedure followed was the same as in the preparat-

ion of 3,4-dimethylbenzhydrol. The 2,4-dimethylbenzhydrol boiled at 166 - 167° (3 mm.); yield, 87%. The oil did not solidify but finally became opaque.

(c) 4-m-Xylylphenylmethyl Bromide (5).

The procedure followed was the same as in the preparation of 3-o-xylylphenylmethyl bromide. The bromide boiled at 184 - 189° (11 mm.); yield, 75%. It was used at once, without analysis for bromine, in the preparation of the pentaarylethane.

(d) 1,1,1,2-Tetraphenyl-2(4-m-xylyl)ethane.

The procedure followed was the same as in the preparation of 1,1,1,2-tetraphenyl-2(3-o-xylyl)ethane. The pentaarylethane was recrystallized twice from a benzene-ethanol mixture, and dried in vacuo at 100° until a carbon-hydrogen analysis showed no solvent of crystallization to be present; yield, 35%; m.p., 171 - 183° dec. in air.

Anal. Calc'd. for $C_{34}H_{30}$: C, 93.09; H, 6.91

Found: C, 92.53; H, 7.19.

VI. Rate Measurements. (7).

The iodine solution was made up by adding o-dichlorobenzene to a solution of 6.5 g. of iodine in 32.5 cc. of pyridine until the total volume was 500 cc.

The sodium thiosulfate solution was made slightly stronger than 0.1 N so that it would be strong enough to react with all of the iodine originally present in the organic iodine solution.

The aqueous iodine solution was made up to 0.1 N in strength and standardized against arsenious oxide.

The samples (0.1025 g. each) of pentaarylethane were weighed into glass vials, 12 mm. deep and 8 mm. in diameter, having flat bottoms. Ten cubic centimeters of the organic iodine solution and 1 cc. of absolute alcohol were placed in a 125-cc. Erlenmyer flask bearing a glass stopper. The flask was suspended in an oil bath kept at 80° to within 0.1°. The vial containing the sample of pentaarylethane was then lowered in an upright position into the Erlenmyer flask by means of forceps and allowed to float on the surface of the organic solution of iodine. The flask after being stoppered loosely was allowed to reach the temperature of the bath, for which ten minutes proved to be sufficient. The vial was then tipped over by swirling the flask, a stop-watch being started at this time. When the desired interval of time had elapsed, the flask was removed from the bath and immersed in ice-water, the watch being stopped at this point.

The flask was kept in the ice water for one minute and then 10 cc. of the sodium thiosulfate solution added. The solution was well mixed for half a minute, the sides of the flask washed down with 50 cc. of water and the excess sodium thiosulfate titrated with the standardized 0.1 N solution of iodine. From the volume of this standard iodine solution needed to give the end-point with starch (3 cc. of a 1% solution) was subtracted the volume of iodine solution required to give the end-point to a

blank. The latter was run with all of the reagents present except the pentaarylethane in exactly the same manner as the regular run. The difference was the volume of 0.1 N iodine which reacted with the radicals formed by dissociation of the pentaarylethane.

Knowing the concentration of the standardized iodine solution, the volume theoretically absorbed by 0.1025 g. of the pentaarylethane was calculated. Calculations were then carried out and values for t plotted against $-\log(1 - Z)$. The best-fitting straight line was drawn, its slope determined, and the "half-life" period calculated. In Table 5. are shown typical data obtained in a representative experiment.

Table 5.

Typical Data Obtained in a Representative Experiment

Wt., 1,1,1,2-Tetraphenyl-2(4-o-xylyl)ethane, 0.1025 g.

o-Dichlorobenzene, 89.3%; pyridine, 4.7%; ethanol, 6%.

Theoretical absorption of 0.0990 N iodine, 4.78 cc.

Temp., 80.0 ± 0.1°.

Time, Min.	0.1 N iodine absorbed, cc.	Z(Found)	-log(1 - Z)
1	0.04	0.0084	0.0036
2	.15	.0314	.0138
3	.19	.0407	.0191
4	.25	.0523	.0234
5	.36	.0753	.0340
6	.41	.0858	.0390
7	.47	.0983	.0450
8	.57	.1192	.0551
10	.63	.1318	.0614

Time was plotted against -log(1 - Z) and the best-fitting straight line drawn.

Slope of line = (0.0644 - 0.0066)/(10-1) = 0.006422/min.

Rate constant = k = 2.3(0.006422) = 0.01477/min.

"Half-life" period = $t_{\frac{1}{2}}$ = 2.3(0.3010)/0.01477 = 46.9 minutes.

Summary

Four new pentaarylethanes were prepared and their rates of dissociation into free radicals were measured by the iodine reaction. From the "half-life" periods obtained, it was seen that the shifting of two methyl groups to different locations on one benzene ring attached to the diarylmethyl carbon resulted in varying degrees of influence on the rate of dissociation into free radicals.

The short "half-life" period of 1,1,1,2-tetraphenyl-2(3-o-xylyl)ethane substantiated the extreme reactivity of 1,2,9,10-tetramethylanthracene.

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